Internal Oxidation and Nitridation of Hot Rolled Steels - A Theoretical Study and its Experimental Verification

Max-Planck-Institut für Eisenforschung GmbH

Gunnar Eriksson Symposium &

GTT-Technologies Annual Workshop and Users' Meeting

Herzogenrath-Kohlscheid (Aachen, Germany)

Christian Doppler Forschungsgesellschaft

12th July, 2012

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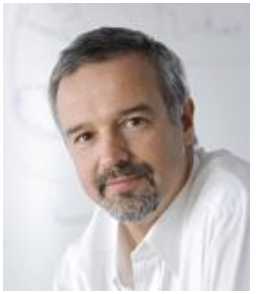
Where we work…

Max-Planck-Institut für Eisenforschung GmbH

Head: Prof. Dierk Raabe



Founded in 1917 from the “Kaiser Wilhelm Institute” by Fritz Wüst.

<u>3 Departments:</u>

- Computational Materials Design
- Interface Chemistry and Surface Engineering
- Microstructure Physics and Alloy Design

Outlook

- Motivation
- Theoretical Calculations
  - Programme Algorithm and Possibilities
  - Oxygen and Nitrogen Diffusion
- Some Examples
  - HT-Corrosion in binary and ternary Alloys
  - Important Modelling Effects
- Conclusion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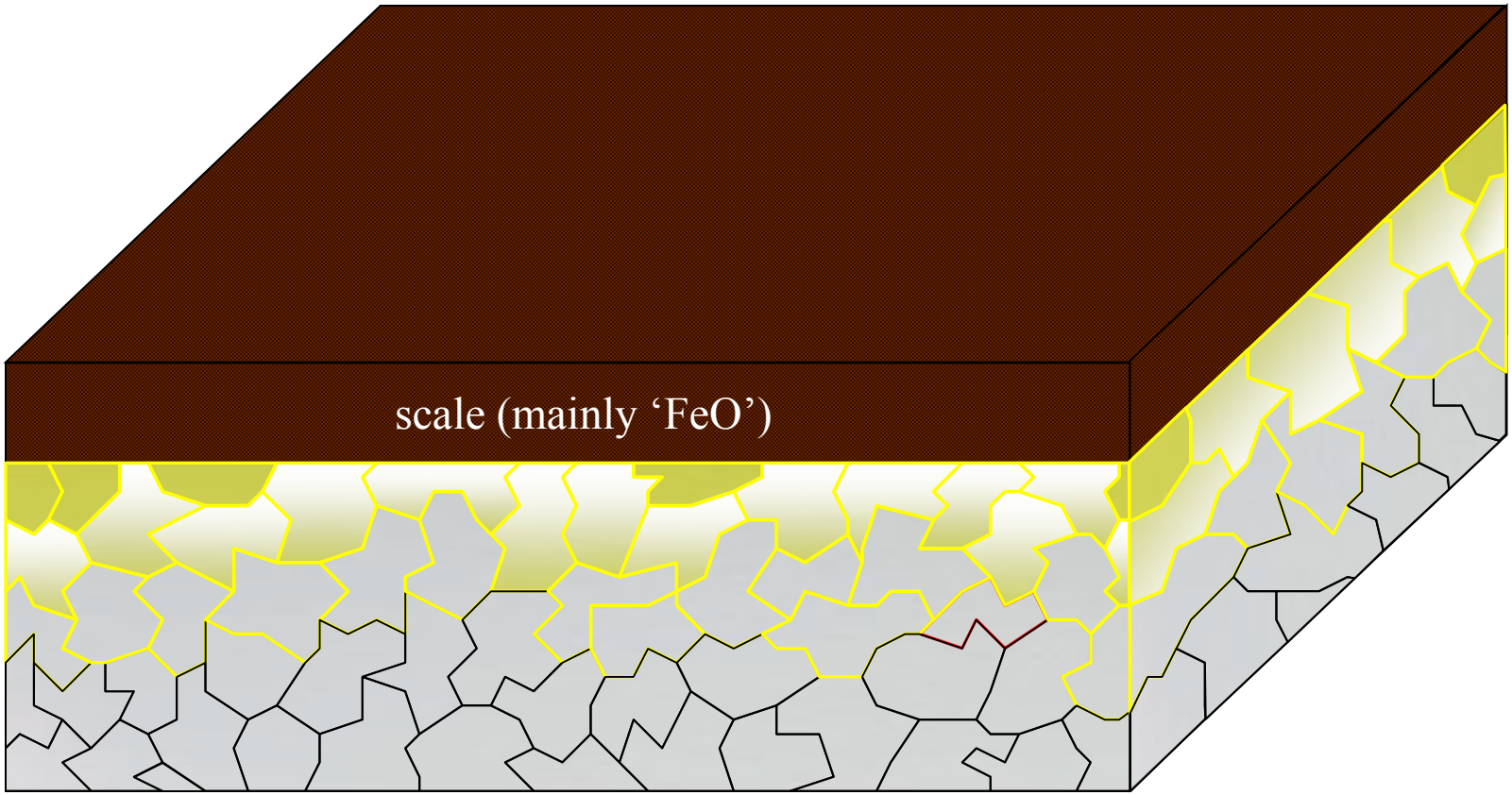
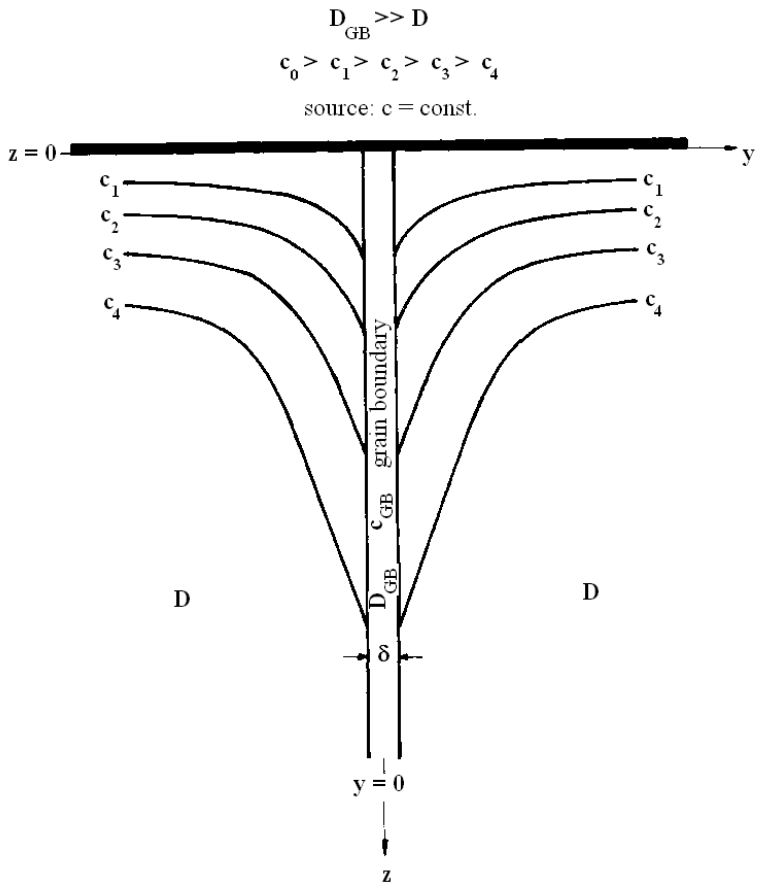
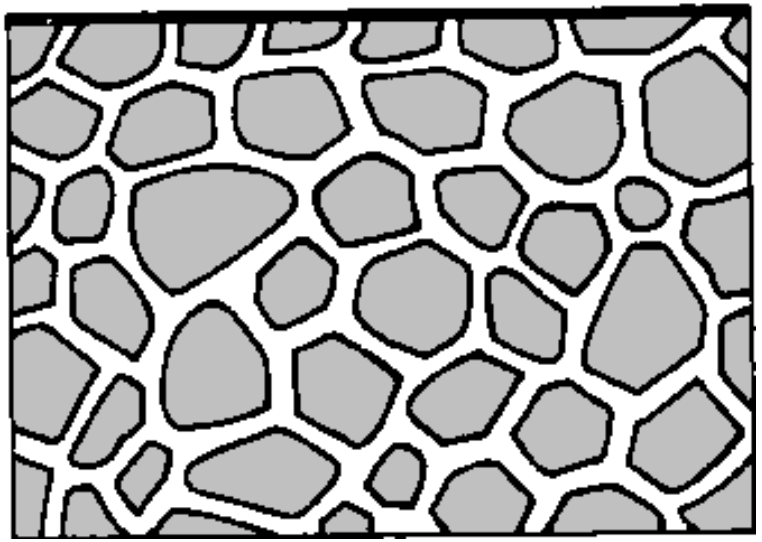
Oxidation Processes in Steel Sheets



Fisher's Model of Diffusion





Whipple – Le Claire equation

$$s\,\delta\,D_{GB} = 0.3292\sqrt{\frac{D}{t}}\left(\frac{\partial \log \bar{c}}{\partial z^{6/5}}\right)^{-\frac{5}{3}}$$

Levine – MacCallum equation

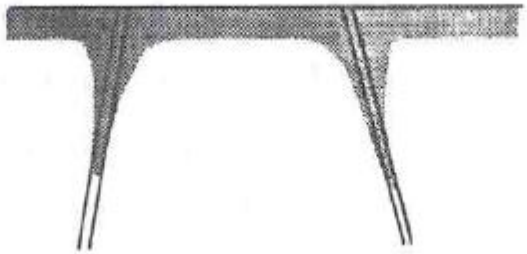
$$s\,\delta\,D_{GB} = 0.4704\sqrt{\frac{D}{t}}\left(\frac{\partial \log \bar{c}}{\partial z^{6/5}}\right)^{-\frac{5}{3}}$$

I. Kaur *"Fundamentals of … Boundary Diffusion" WILEY (1995)*

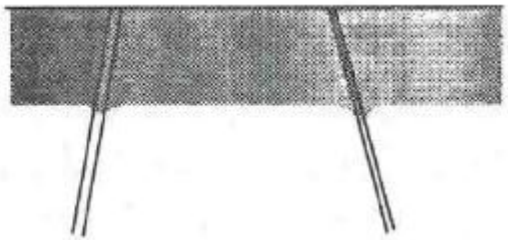
Grain Boundary Diffusion Regimes

Coarse grained

C – regime

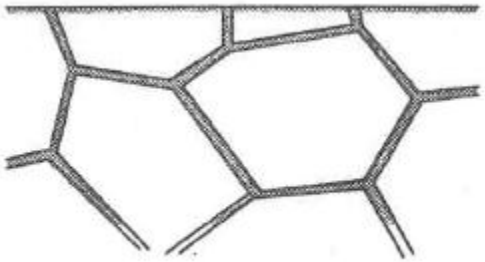


B – regime

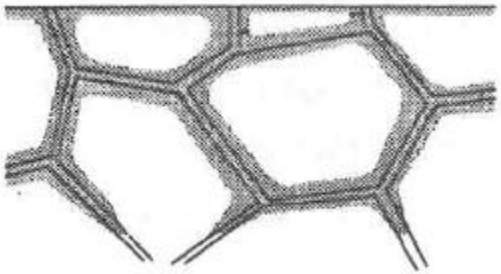


A – regime

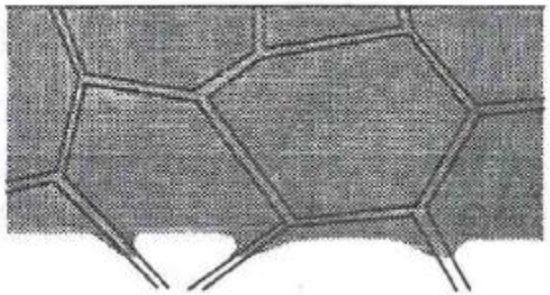
Fine grained



C' – regime



B' – regime



A' – regime

Figure: Illustration of different diffusion regimes, depending on total diffusion time and ratio of D_{GB}/D.

I. Kaur *"Fundamentals of … Boundary Diffusion" WILEY (1995)*

Some Published Works on HT-Corrosion

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DOI: 10.1361/154770305X66592
1547-7037/$19.00 ©ASM International

Internal Corrosion of Engineering Alloys: Experiment and Computer Simulation

Ulrich Krupp and Hans J. Christ

(Submitted July 18, 2005)

High-temperature corrosion is generally known as a material degradation process that occurs at the surface of engineering components. In the case of internal corrosion, the corrosive species penetrates into the material by solid-state diffusion leading to the formation of internal precipitates, for instance, oxides (internal oxidation), nitrides (internal nitridation), and carbides (carburization). It is known from numerous publications and technical failure cases that internal corrosion results in a strong deterioration of the properties of a material (i.e., near-surface embrittlement or the dissolution of strengthening phases). The present article introduces the classic theory of internal oxidation and reviews some recent research on internal corrosion phenomena that are closely related to the failure mechanisms of thermally grown protective oxide scales on several commercial high-temperature alloys (e.g., single-crystalline and polycrystalline Ni-base alloys and Cr steels). The mechanisms and kinetics of internal corrosion processes are determined by the temperature, the local chemical composition of the material, the solubility and diffusivity of the corrosive species, as well as the mechanical loading conditions. These influence factors are taken into account by means of a computer model combining a numerical finite-difference approach to solve the diffusion differential equations with the thermodynamic tool ChemApp. Using several examples, it is shown that the model has been applied successfully to simulate the internal nitridation, carburization, and oxidation of high-temperature alloys.

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Temperature
in Ar–H_2–H_2

D.J. Young[a], J. Zu

Departm [a]School of Materials Scienc
[b]Forschungszentrum Jülich,

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C. Oxidation

Abstract

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parabolic oxide-layer growth r

Keywords: Modelling; Thermodyn

self-diff

1. Introduction

Internal corrosion is a generic kind of material degradation occurring at high temperatures that is driven by the inward diffusion of a corrosive species (i.e., oxygen, nitrogen, carbon, or sulfur, followed by internal precipitation of the respective oxides, nitrides, carbides, and sulfides).[1] Contrary to the formation of superficial scales, which in the case of Cr_2O_3 and Al_2O_3 protect the substrate against excessive corrosion attack,[2] internal corrosion may result in a deep deterioration of the physical properties of the material (e.g., creep resistance and high-temperature fatigue strength).[3,4] Figure 1 shows an example of internal oxidation (Al_2O_3) and nitridation (AlN; penetration depth ξ = 600 μm) underneath a thin Cr_2O_3 scale.

The mechanism of internal corrosion depends on the local concentrations and the diffusivities of the corrosive species and the metallic elements in the substrate. For the example shown in Fig. 1, a low oxygen partial pressure, $p(O_2)$, relative to the nitrogen partial pressure $p(N_2)$ in the combustion gas leads to conditions in the material interior, for

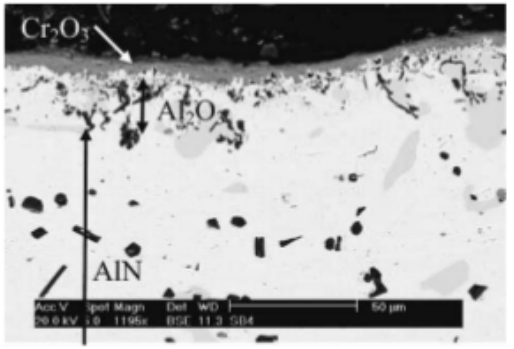


Fig. 1 Internal oxidation and nitridation attack of a failed natural gas burner tube of alloy 601 operated at T = 1100 °C

which AlN instead of Al_2O_3 is the thermodynamically most stable compound.*

Even in the case of Al_2O_3-scale-forming Ni-base super-

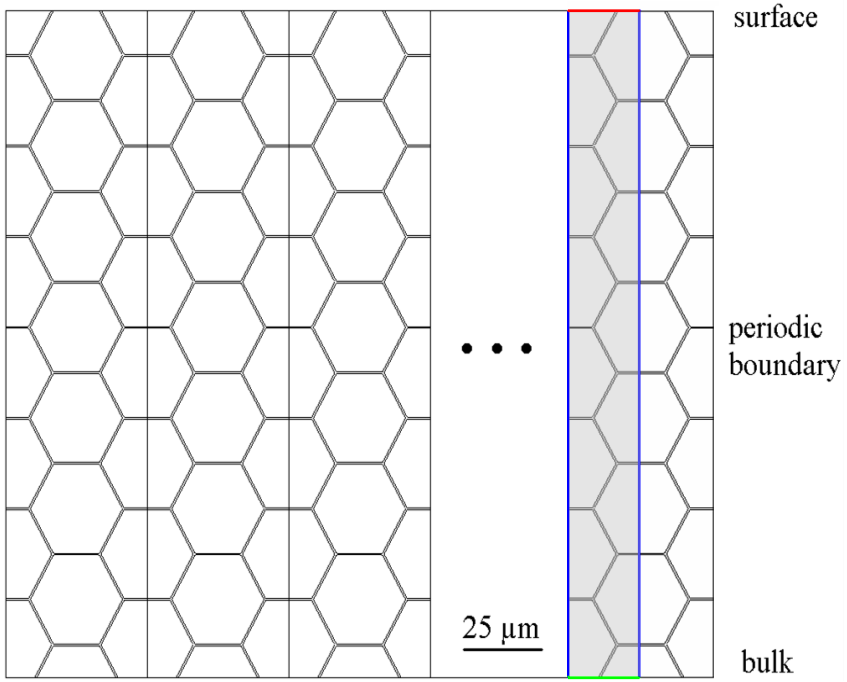
Programme Algorithm

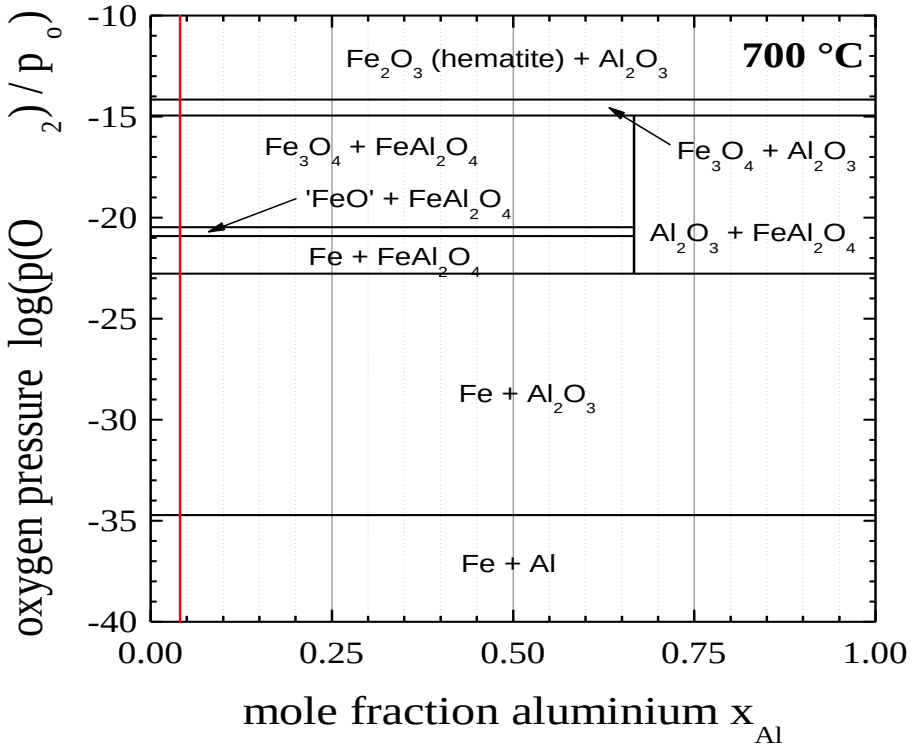
element migration

chemical reaction

$$\frac{dc_{i(x,t)}}{dt} = \mathrm{div}\left(D_{i(x,T)}.\nabla c_{i(x,t)}\right)$$

CHEMAPP





ASTRID, published in *Oxid. Met.* **76** (2011) 247

Data Handling

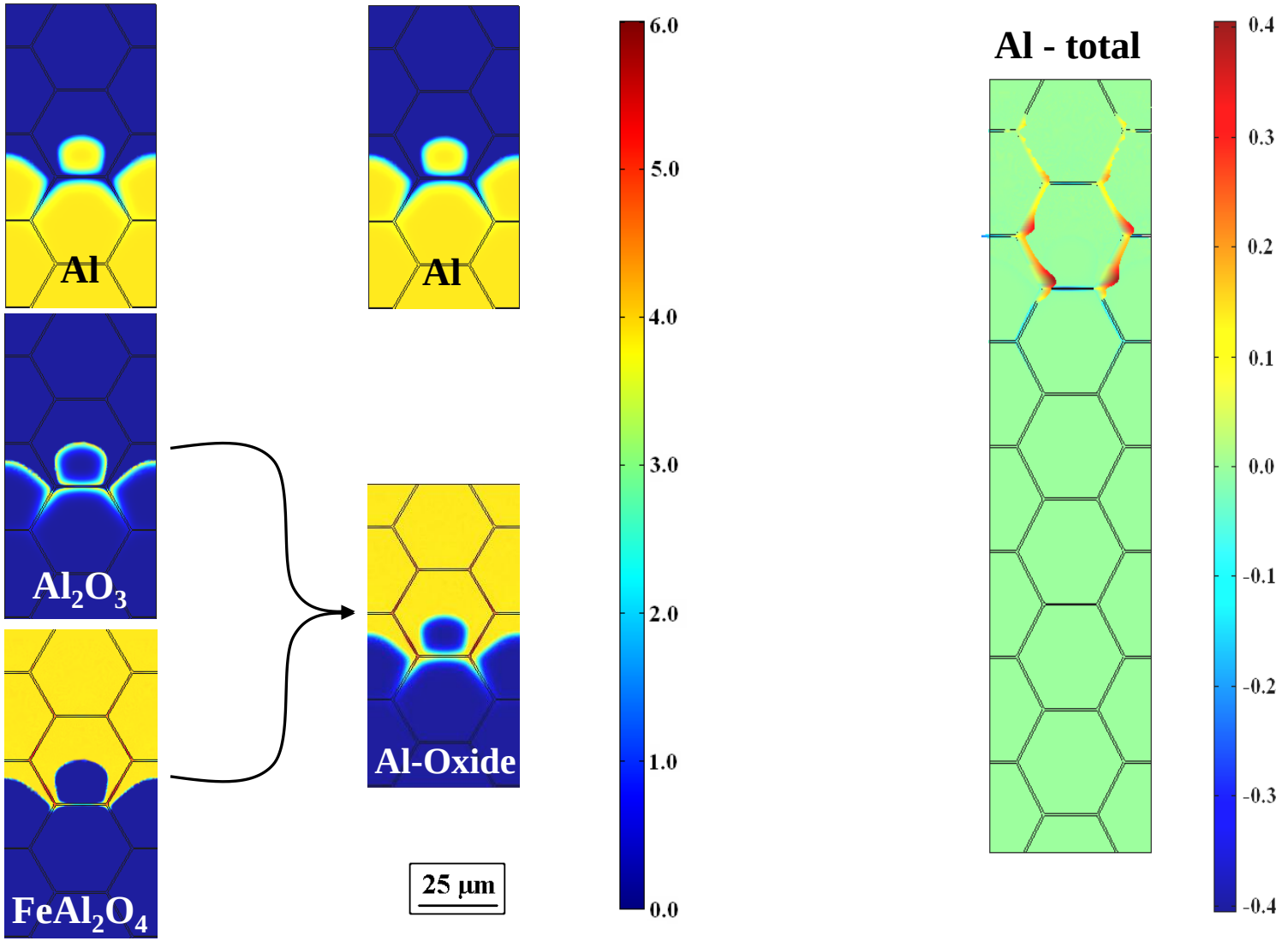
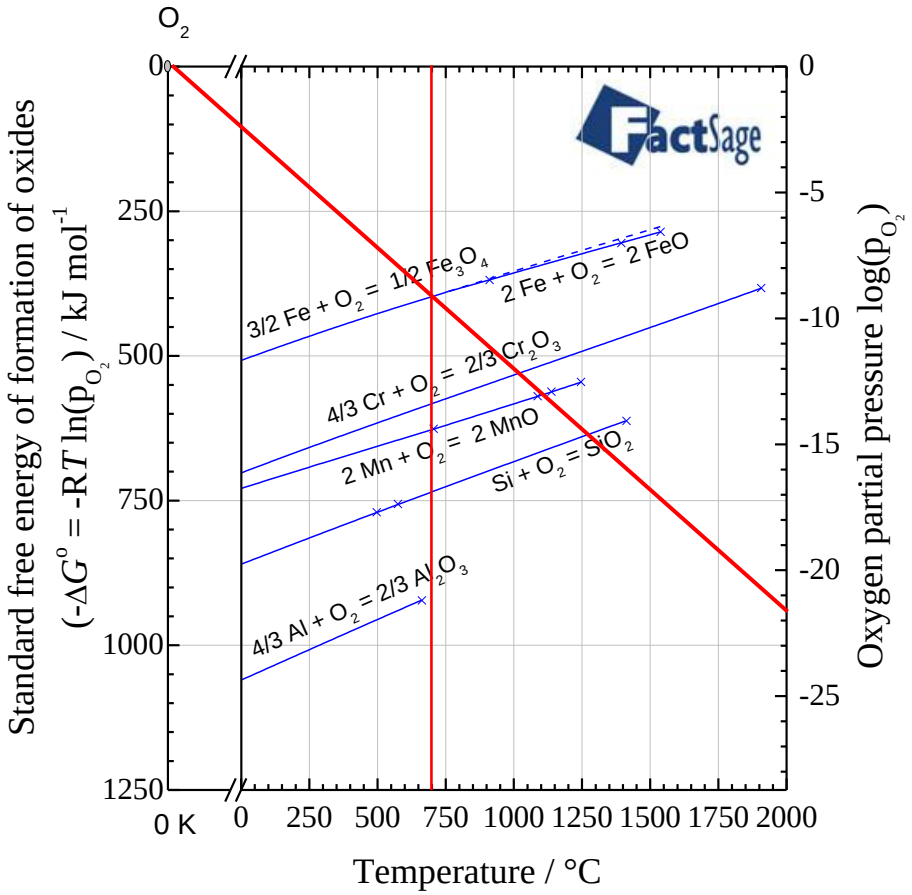


Figure: Spatial phase distributions of Fe, 2 wt-% Al (4.05 mol-% Al) after oxidation at $p(O_2) = 10^{-22}$ bar for 60 min at 700 °C.

Oxide Stability



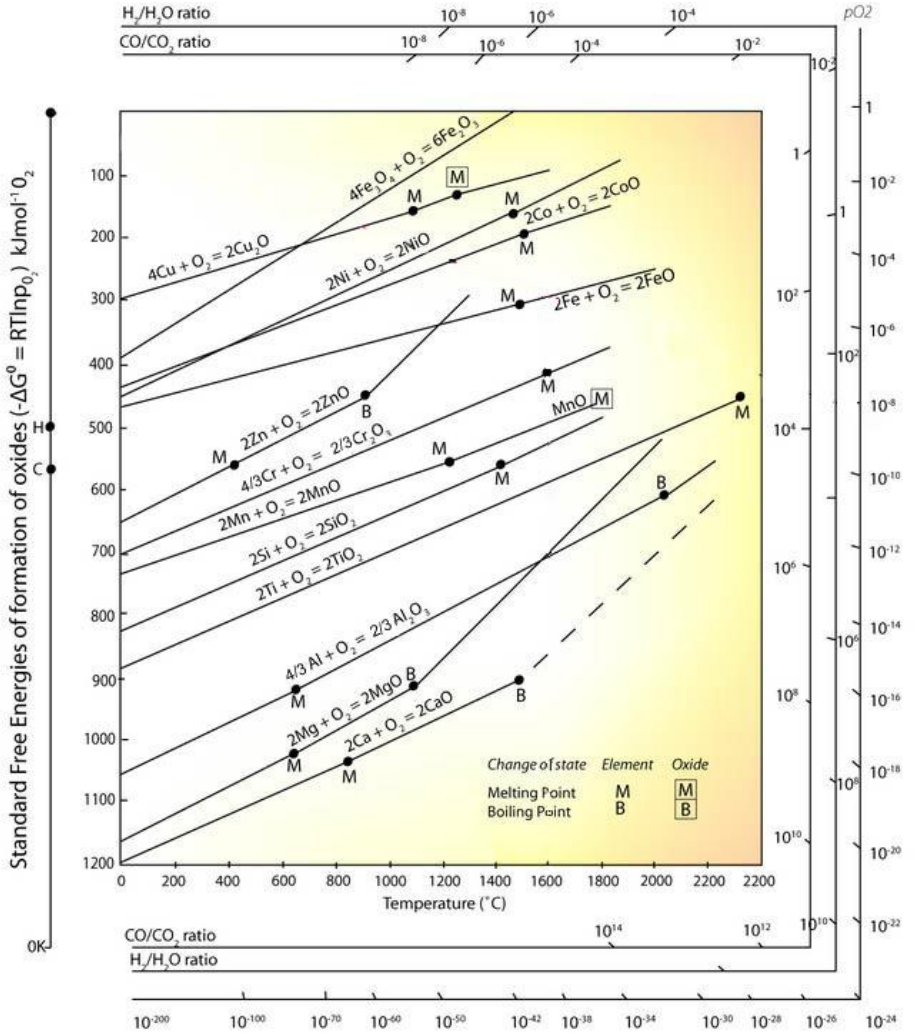


Figure: Calculated and experimentally determined Ellingham-Diagrams for the Oxide Stability of Iron, Chromium, Manganese, Silicon and Aluminium.

figures from FACTSage (left) and ww.doitpoms.ac.uk (right)

Iron – Manganese – Chromium alloy

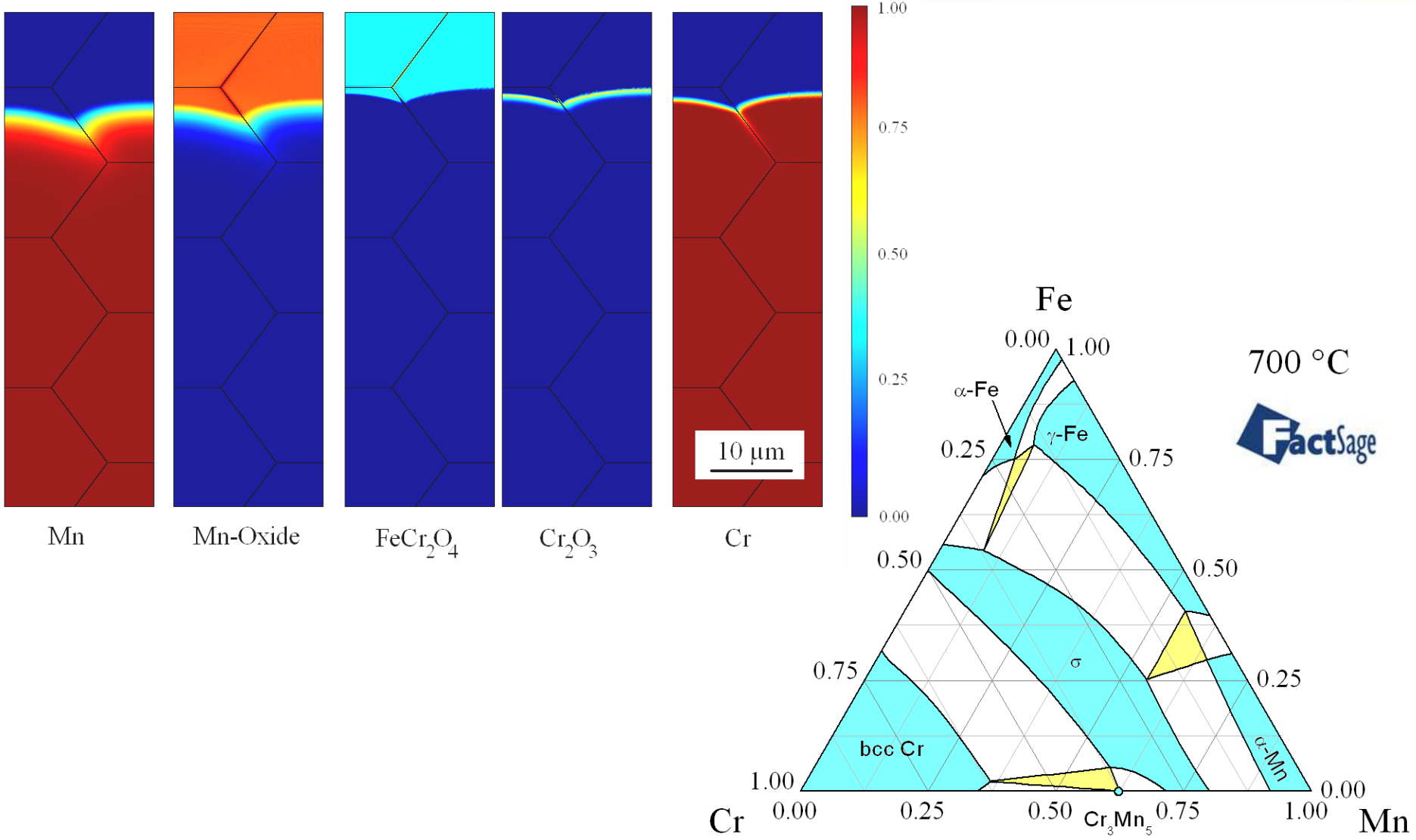
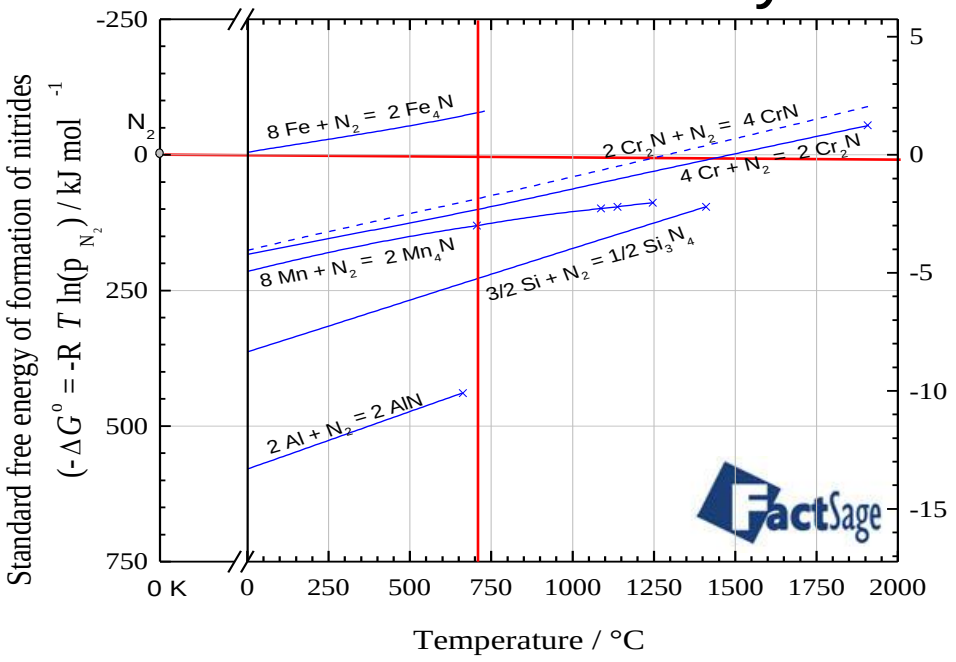


Figure: Spatial phase distribution in an Fe, 2 wt-% Mn, 0.8 wt-% Cr alloy after oxidation at $p(O_2)= 3 \cdot 10^{-22}$ bar and 700 °C for 120 min and ternary phase diagram.

published in *Mater. Sci. Forum* **969** (2011) p.76

Properties of Nitrogen

Nitride Stability



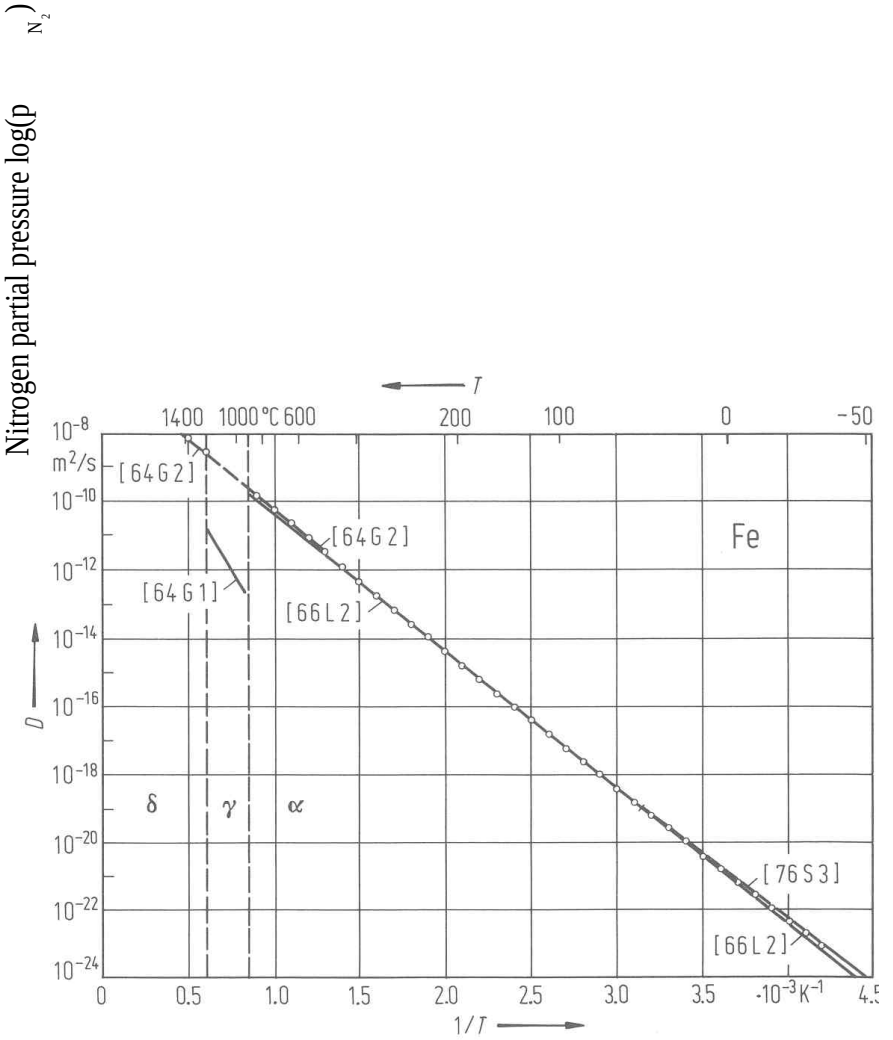
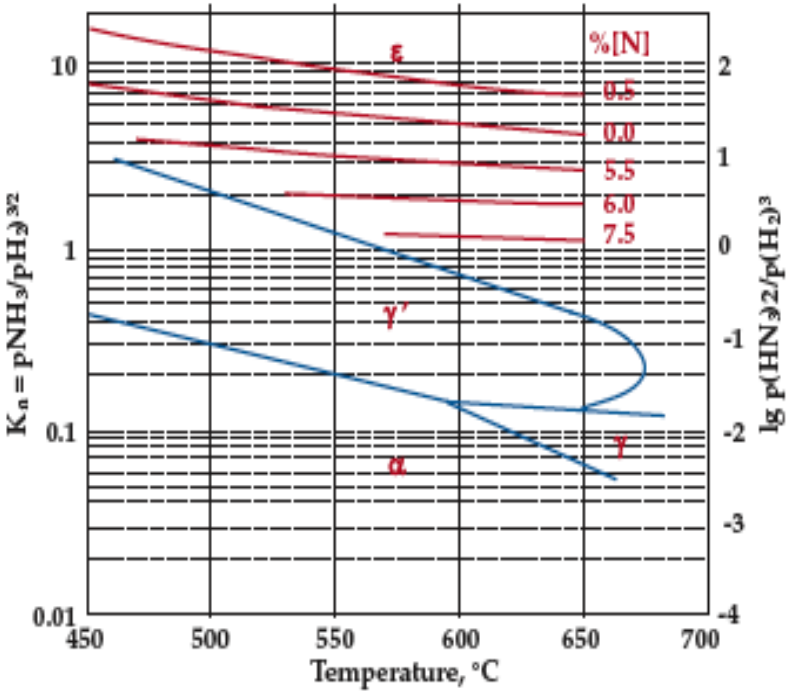


Fig. 22. Fe. Diffusion coefficient for N diffusion in α, γ and δ-phase Fe vs. (reciprocal) temperature. Circles: calculated from equation quoted from [76S3].

figures from Landoldt-Börnstein (right) and FACTSage (left)

Theoretical Principles



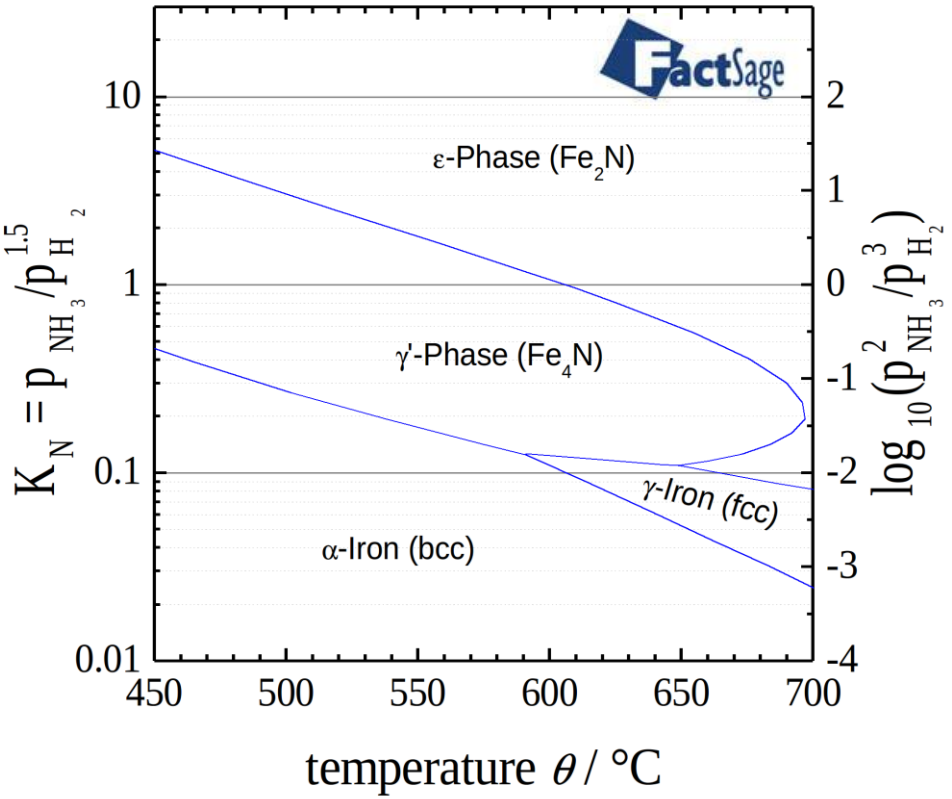
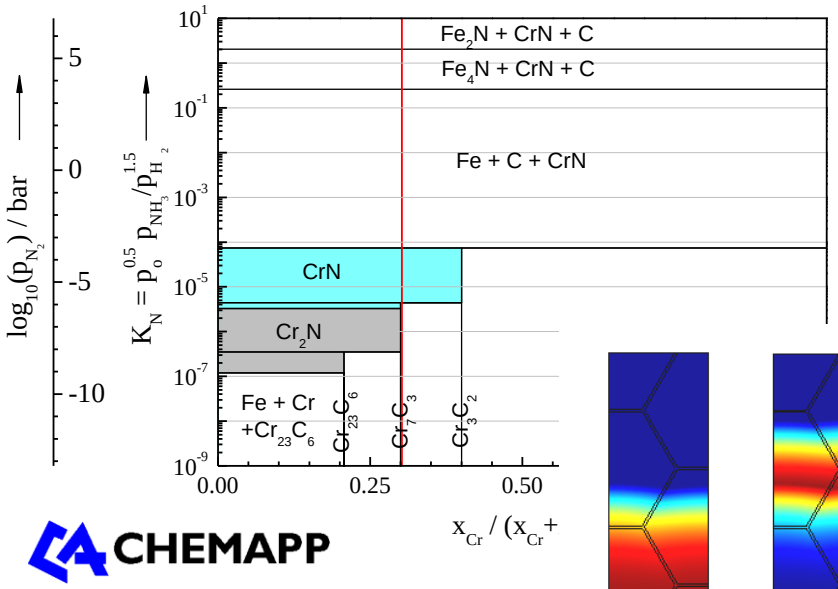


Figure: Lehrer-Diagram of iron nitrides according to literature (left) and calculated with the programme FactSage (right).

Iron – Chromium – Carbon alloy



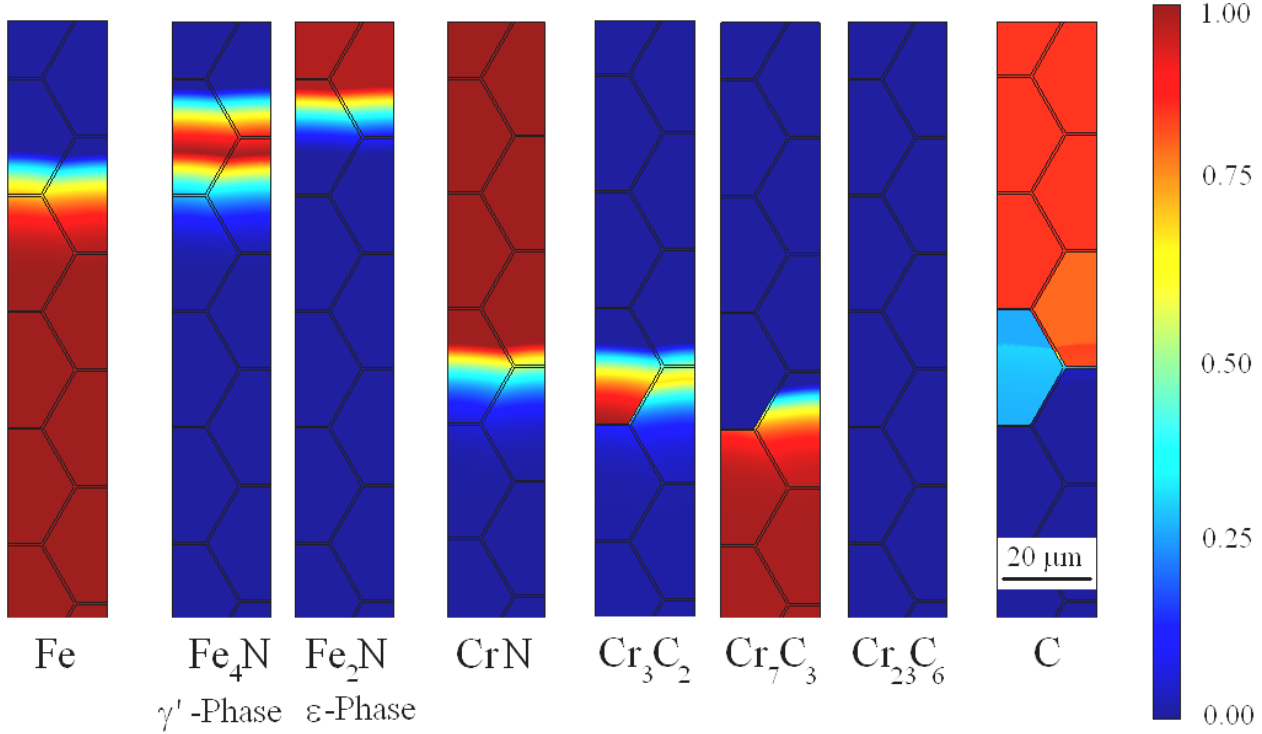


Figure: Spatial phase distribution in an Fe, 1 wt-% Cr, 0.1 wt-% C alloy after gas nitriding at K_N= 2.4 and 500 °C for 48 h and phase stability diagram.

published in *HTM J. Heat Treatm. Mat.* **66** (2011) p.100

Comparison of the SAE51xx steels

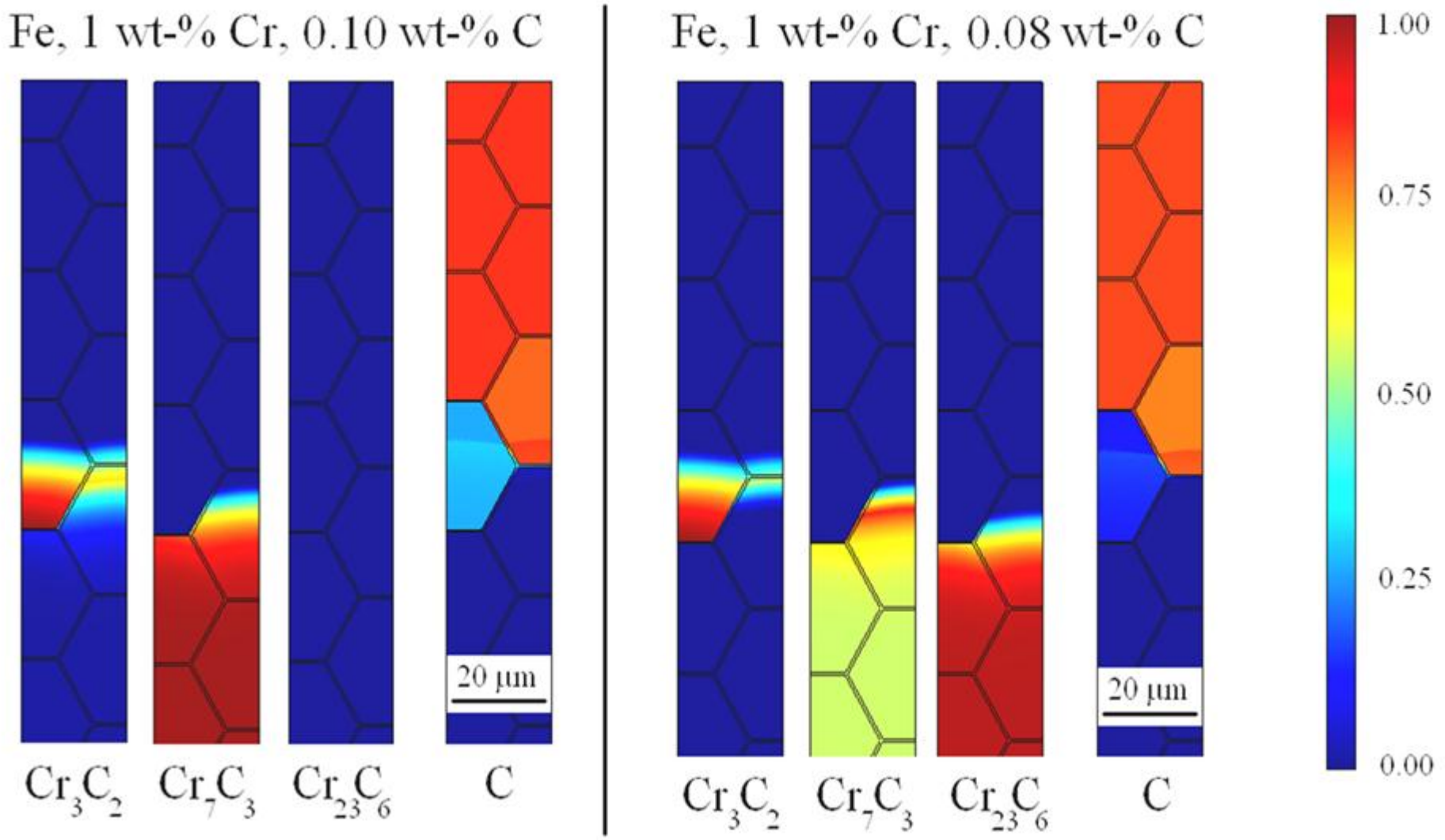


Figure: Comparison of the carbide phase distribution in two SAE51xx type steels after gaseous nitriding at K_N = 1 000 (p_{tot}= 1 atm) and 500 °C for 48 h.

„Real“ Steels

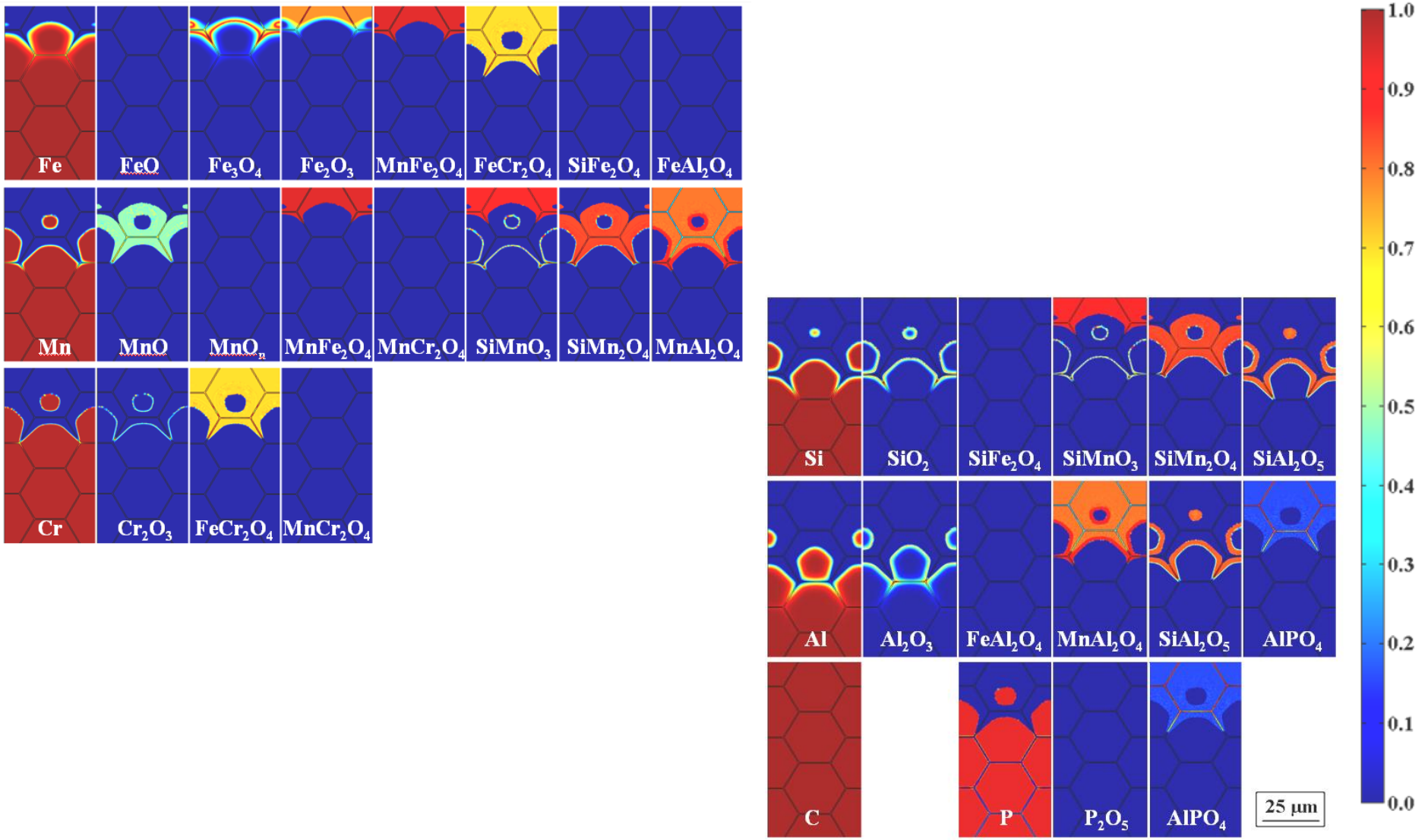


Figure: Calculated phase distribution of an industrial steel alloy after oxidation at $p(O_2) = 10^{-22}$ bar and a technical cooling programme.

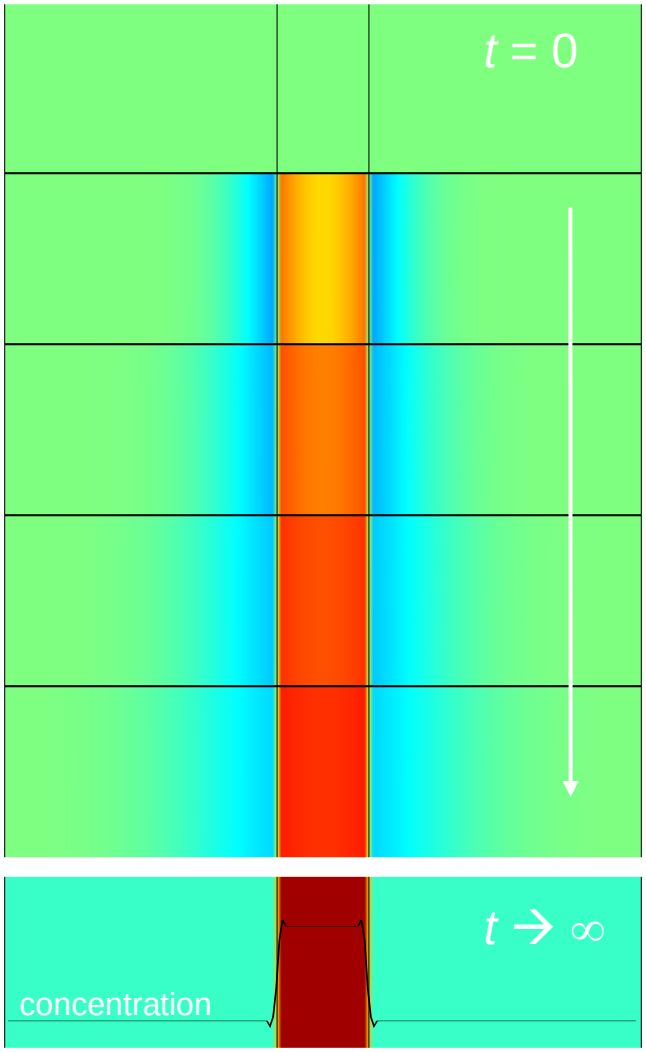
Diffusion between different Phases

$$J_A = -D\,\nabla c \qquad J_A = -L\,\nabla \mu$$

$$J_A = -L\,\nabla\mu = -L\,\frac{\partial \mu}{\partial c}\nabla c = \cdots = -\underbrace{L\frac{RT}{c}}_{D}\nabla c - L\left(\nabla \mu^o + \frac{RT}{\gamma}\nabla\gamma\right)$$

Figures: Shibuya (渋谷) crossing in Tokyo with green and red pedestrian lights.

Segregation



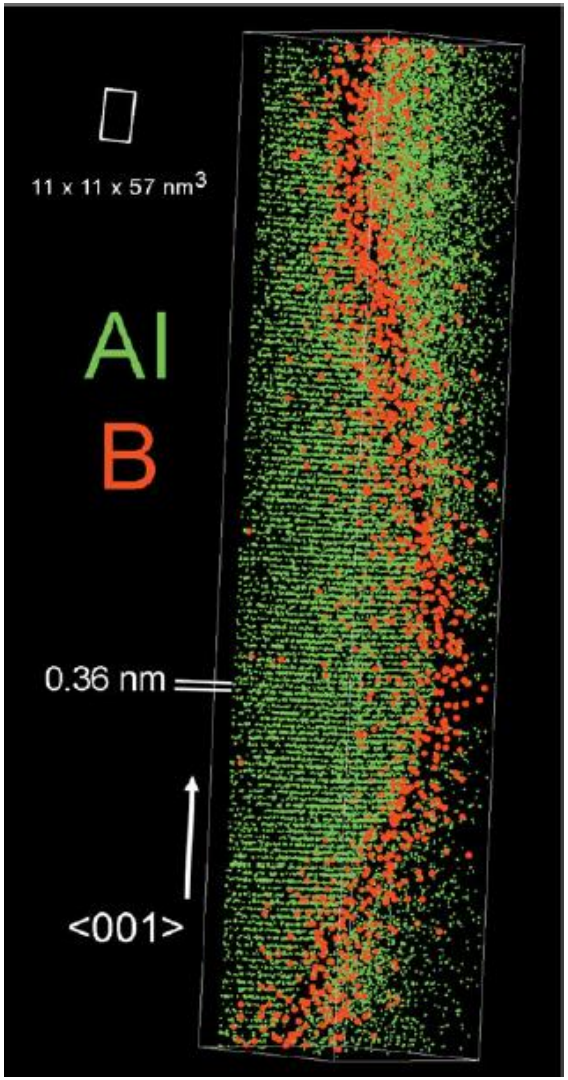
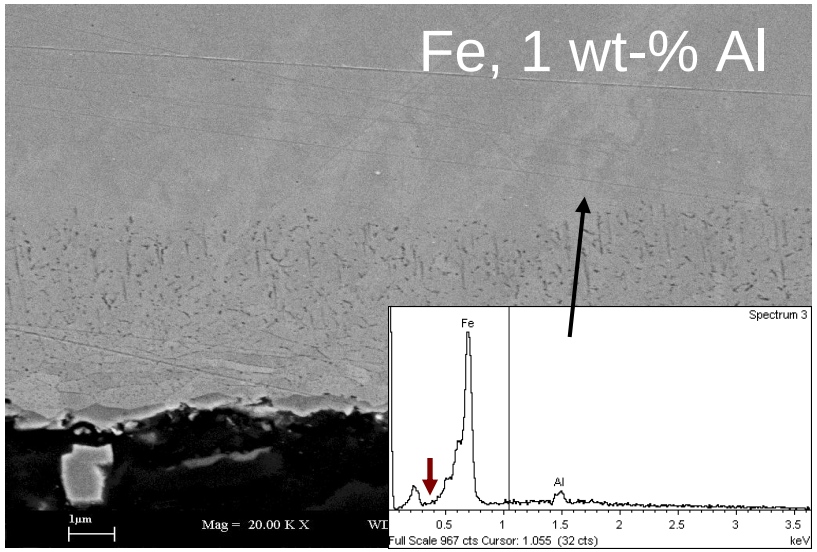
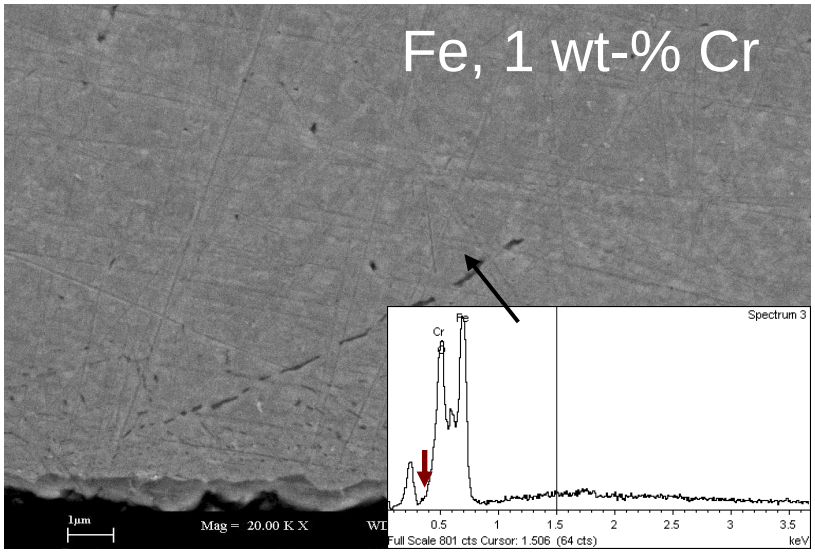


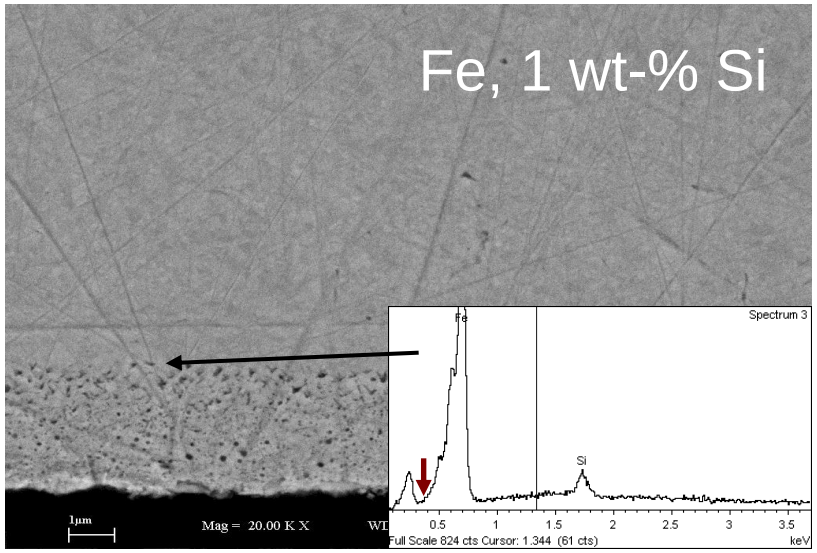
Figure: Numerical simulation of segregation (left) and 3D atom probe tomography of segregated boron atoms along the grain boundary in a NiAl superalloy [1] (right).

[1] Blavette et al. *Microsc. Microanal.* **13** (2007) 464

Binary Iron Alloys







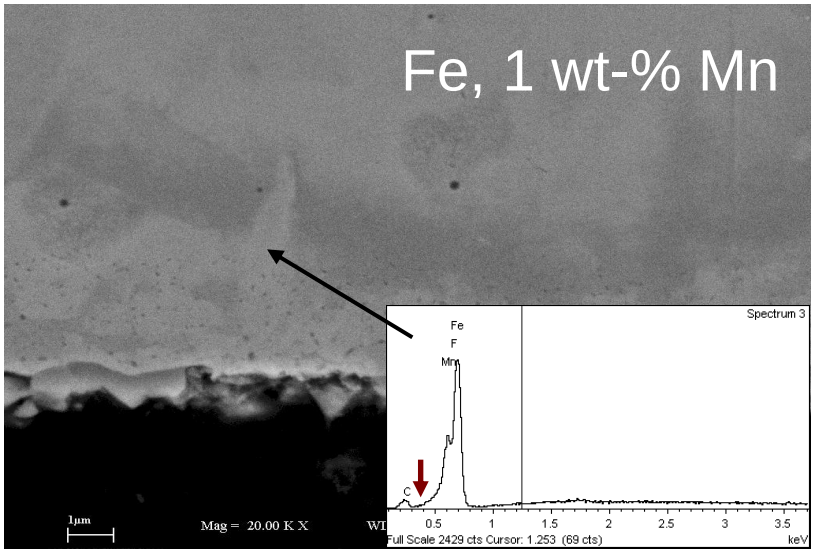


Figure: SEM and EDX-images of four different binary iron alloys, oxidised at 700 °C for 5 h in N_2 / 2.5 % H_2 / H_2O (DP +8 °C). The red arrow marks the N signal position.

Cross Section

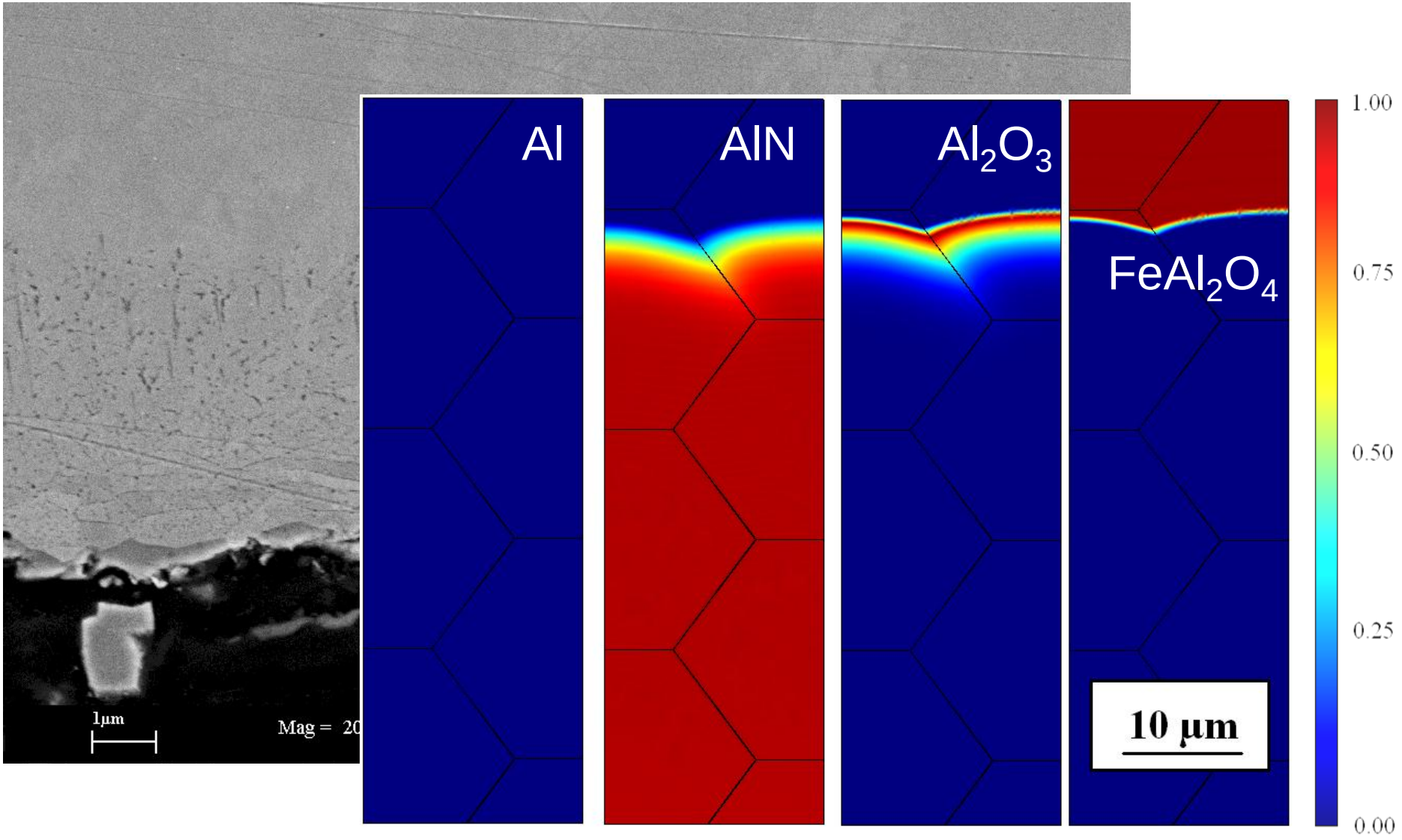


Figure: Fe, 1wt-%Al, oxidised at 700 °C for 5 h in N_2 / 2.5 vol-% H_2 / H_2O (DP +8 °C). SEM-picture (left) and numerical simulation of the phase distribution (right).

Summary

- Reaction-Diffusion-Systems provide a powerful method to describe High Temperature Processes
- FactSage and ChemApp proved to be a valuable tool for making theoretical assumptions
- Good agreement with experimental values for oxidation depth and oxide formation
- Deviations between theory and experiment can be used to foster further research

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